Unit 3: Chemical Calculations – Tutorial 6

Stoichiometry

Determining the stoichiometry of acid base reaction

First, it is required to find the basicity of the acid and acidity of base. They are exchangeable H^+ and OH^- ions respectively. Then these numbers are exchanged to provide the stoichiometry.

Acid and the Base	Stoichiometry
1. HCl + $NaOH$	1:1
2. $Al(OH)_3$ + H_2SO_4	2:3
3. $NaOH$ + H_3PO_2	1:1
4. $Ba(OH)_2$ + CH_3COOH	1:2
5. $Ca(OH)_2$ + H_2SO_4	1:1

Limiting reagent

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1. 1.08 g of Al metal was reacted with 250 mL of 0.4 mol dm^{-3} HNO_3 solution.
   a. What is the limiting reagent

   b. Calculate the mols of remaining reactant

   c. What is volume of the gas evolved at STP?

d. Calculate the concentration of NO_3^- in the solution in ppm.

2. 50 mL H_2SO_4 solution which is provided has a density of 0.196 g cm^{-3} also contains 60% purity by mass percentage. This solution was reacted with 200 mL of 0.1 mol dm^{-3} KOH solution.
   a. Determine the limiting reagent.

   b. Calculate the remaining concentration of the reactant.

   c. Calculate the concentration of the resulting K^+ salt in the units of ppm.

3. Which species is suitable as a primary standard to carry out an acid base reaction.
   a. $Mg(OH)_2$ b. $MgCO_3$ c. NaOH d. Na_2CO_3 e. KOH

Reason

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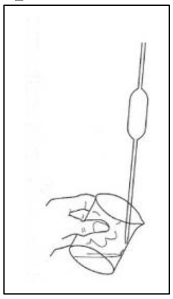
Determining the stoichiometry of a reaction using titrimetric method

Out of many titrimetric methods 3 methods are focused.

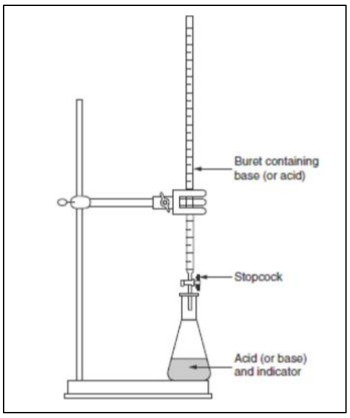
- Acid base titrations
- Redox Titrations
- Iodometric titrations

Acid base titrations

Pipette



- Is used to measure a desired amount of the sample
- First use HNO_3 to clean and then wash with copious amounts of water.
- Pipette fillers are used to pipette out the liquid
- There should be no air bubbles in it
- The reading should be taken at the calibrated temperature
- Meniscus should be adjusted by taking the pipette end out of the liquid
- The last drop remaining in the pipette should not be removed by blowing it out.
- The liquid is transferred by keeping the pipette vertical and the titration flask in an angel.



Burette

- This is used to measure a specific volume of the solution.
- The burette is calibrated from top to bottom
- First cleaned with an acid, then with water and later with the solution used to titrate.
- The volume of a single drop is the smallest volume = 0.05 cm^3.
- It is not necessary to have the initial reading 0 cm^3 whenever a reading is taken.

Titration flask

- Solutions added from the pipette is kept in the titration flask and it should never be washed with an acid or base.

Consider the following techniques and suggest whether there is an error introduced to the titration by following them.

Technique followed	Whether the burette reading increases of decreases	Reason
1. Washing off the inner walls of the titration flask near the end point using distilled water.		
2. Adding few ice cubes to avoid heating up the solution in the titration flask		

3. Some air bubbles get trapped inside the burette.		
4. The region below the stopper of the burette is not filled with the liquid.		
5. Burette is washed only with water before filling the reagent into the burette.		
6. Blowing the last drop of the liquid trapped inside the pipette into the titration flask.		
7. Titration flask is washed with distilled water and washed with the liquid that is measured into the titration flask		
8. Pipette is washed only with water and the solution is pipetted out.		
9. Some air bubbles get trapped inside the pipette.		

10. The meniscus of the liquid in pipette is not in the calibration mark.		

Consider the statements given below and state whether the two statements correct, incorrect and whether the second statement explains the first statement.

	First statement	Second statement
1	A specific volume of liquid can be measured using the pipette.	All pipettes have a specific volume that can be measured, marked on the body.
2	A pipette must never be washed with the liquid that is to be measured.	Pipette can be washed with HNO_3 as a step to clean inside.
3	Trapping air bubbles inside a pipette does not affect the reading of the titration.	Trapping air bubbles leads to add a smaller volume of liquid into the titration flask.
4	There is a small amount of liquid trapped inside a pipette due to the capillary effect.	When adjusting the meniscus of the pipette, it is important to immerse the other end of the pipette inside the liquid which is to be measured.
5	If the liquid is measured into pipette at a temperature than the temperature specified on the body of the pipette a higher volume of the liquid can be measured.	If the liquid is pipetted out at the temperature specified, the burette reading would be lower than the real value.
6	The liquid remaining in the pipette should be carefully added into the titration flask.	Certain liquids must be filled into the pipette using a pipette filler.
7	Burette can be used to measure the volume of any liquid.	A burette is graduated from the top to the bottom.
8	Trapping of gas bubbles in the liquid in a burette does not introduce any errors into the titration.	The gas bubbled trapped in the liquid should be first removed before starting the titration.
9	Burette should not be washed with the liquid used for the titration.	Burette should be washed with only distilled water.
10	The volume of a drop of liquid dispensed by a burette is 0.05 mL.	The minimum volume of the liquid that can be measured from the burette is 0.05 mL.

Equivalence point

This is the point of which all the reactant in the titration flask would completely react with reactant that is added from the burette.

End point

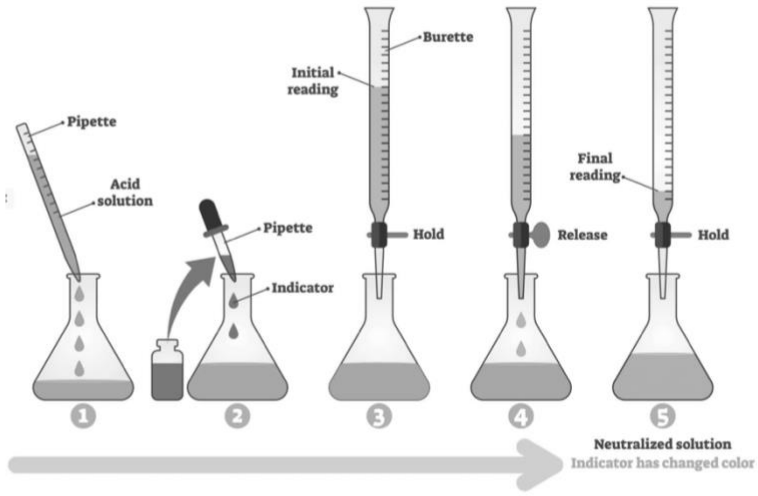
This is point of which the colour change in the titration flask takes place. This point depends on the indicator used.

Indicator

This is usually a dye that shows a different colour in the acidic medium and another colour in the basic medium. Find the colour changes of few indicators used in acid base titrations.

Indicator	Approximate pH Range for Color Change	Color Change
methyl orange	3.1–4.4	red to yellow
bromthymol blue	6.0–7.6	yellow to blue
phenolphthalein	8–9	colorless to pink
litmus	4.5–8.3	red to blue
bromcresol green	3.8–5.4	yellow to blue
thymol blue	8.0–9.6	yellow to blue

Titration of a known volume of 0.1 moldm^{-3} NaOH with 0.1 mol dm^{-3} HCl solution.



- Wash the burette with distilled water and 0.1 mol dm^{-3} HCl solution.
- Fill the burette with 0.1 mol dm^{-3} HCl solution up to 0.00 mL mark without trapping any air bubbles.
- Wash the titration flask with distilled water.
- Wash the pipette with distilled water and 0.1 mol dm^{-3} NaOH solution. Pipette out 25.00 mL of the 0.1 mol dm^{-3} NaOH and transfer it to the titration flask.
- Add few drops of phenolphthalein. The solution becomes pink in colour.
- Keeping a white background, add HCl into the titration flask by opening the outlet of the burette while swirling the titration flask.
- Stop adding HCl when the colour changes from pink to colourless.
- Titration should be repeated until two consecutive data points are obtained. Use the mean value for the calculation.

Readings

Initial Volume/ mL	Final Volume/mL	Difference/ mL
0.00	25.00	25.00
0.00	25.50	25.50
0.00	24.50	24.50

Volume of HCl consumed = $\frac{25.00+25.50+24.50}{3}$ = 25.00 mL

Improving the confidence in the burette reading.

Following technique is used to improve the confidence in the burette reading.

1. If the three burette readings are closer to each other, then the average reading of the three is taken.
2. If two burette readings out of the three are the same, then this reading is taken
3. If one of burette readings is considerably off, then that reading is ignored and mean of the other two readings are taken.

Questions

11. **What is the correct statement regarding titrations?**

    1. The acid must be kept in the burette in all acid base titrations.
    2. The initial burette reading must be kept at 0.00 mL at the beginning of all titrations.
    3. The remaining drop of the liquid in the pipette should be always dispensed into the titration flask by carefully blowing off.
    4. An indicator is not required in certain titrations.
    5. If the burette reading of two trials of acid base titration is significantly different, then their average should be taken for the calculation.

12. Which of following is/are step/s to be followed when measuring a given volume of a certain liquid using a pipette?
    1. When the liquid inside the pipette is adjusted to the calibration mark, the tip is pipette should be immersed inside the liquid.
    2. When the liquid is dispensed into the titration flask the tip of the pipette should touch the inner wall of the titration flask.
    3. When transferring the liquid, the pipette is kept vertical and the titration flask in an angle.
    4. The last drop remaining in the pipette after dispensing the liquid must be carefully blown into the titration flask.

13. What us the step that should be essentially followed when 25 mL portion of NaOH is titrated with HCl?
    1. Pipette is to be washed with HCl solution.
    2. Titration flask to be washed with NaOH.
    3. Measing the temperatures of the two liquids used or the titration
    4. HCl solution to be filled till 0.00 mL in the burette.
    5. Inner walls of the burette are to be washed with the HCl solution.

Calculating the volume required to neutralise a given solution with a known concentration.

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14. Calculate the 0.5 mol dm^{-3} volume of NaOH solution required to neutralise 100 mL of 0.4 mol dm^{-3} HNO_3 solution.

15. 20 ml of a NaOH solution prepared by dissolving 1.8 g of NaOH in 200 mL of total solution was pipetted out to dilute up to 100 mL mark. If 10 mL of this solution was titrated, calculate the volume of 0.01 mol dm^{-3} H_2SO_4 required to reach the end point.

16. 11.2 g of KOH is dissolved in water to form 200 mL solution. 10 mL of this solution is dissolved in water and made to the 100 mL mark. Calculate the volume of 0.4 mol dm^{-3} H_2SO_4 required to titrate 20 mL of this solution completely.

17. The mass percentage of NaOH in a mixture that contains only NaOH and $Ba(OH)_2$ is 60%. 2.00 g of this mixture was dissolved in water to prepare a solution of 500 mL. 25 mL of this solution was pipetted out to titrate with 0.1 mol dm^{-3} HNO_3. Calculate volume of HNO_3 needed?

18. 20 mL of 0.2 mol dm^{-3} $Ca(OH)_2$ solution is fully neutralised using 10 mL of HNO_3. Calculate the concentration of the HNO_3 in the solution.

19. 1.43 g of $Na_2CO_3.10H_2O$ dissolved in water to form a volume of 250 mL. 25 mL of this solution is pipetted out and is diluted to 100 mL mark. 10 mL of this solution is titrated using a HNO_3 solution. End point is reached when 25.0 mL of HNO_3 is dispensed. Calculate the concentration of HNO_3.

20. 2 mL of a pure H_3PO_4 solution is diluted to 500 mL by adding distilled water. 34.8 mL of 0.102 mol dm^{-3} is required to completely neutralise 25 mL of this solution. Calculate the density of the initial H_3PO_4 solution. (P =31)

Back titration

- Material in a certain solution is reacted with another compound added to it in excess.
- The amount of the remaining compound is determined using a standard titration.
- By subtracting the mols of the compound, the amount used is determined.
- This data is used to calculate the analyte of interest.

21. 1.5 g of $CaCO_3$ with some contamination was completely dissolved in 10 mL of 0.4 mol dm^{-3} solution. Resulting solution was diluted to 100 mL mark. 25.0 mL of this solution was pipetted out and was titrated with 0.2 mol dm^{-3} NaOH solution. End point was reached when 18.75 mL of NaOH was consumed. Calculate the percentage purity of $CaCO_3$. (Ca = 40, C =12, O=16)

22. 2.70 g of hydrated Na_2CO_3 sample was mixed with 50 mL of 0.50 mol dm^{-3} H_2SO_4 solution and was heated to evolve all CO_2 by heating. 25 mL of the resulting acidic solution was separated out, was titrated with 1 mol dm^{-3} NaOH solution to observe the end point at 10 mL. Calculate the mass percentage of Na_2CO_3 in the sample.

23. 8 mL of 0.75 mol dm^{-3} HCl solution was mixed with 25 mL of K_2CO_3 solution. Resulting acidic solution was neutralised with 15.0 mL of 0.4 mol dm^{-3} H_2SO_4, then calculate the concentration of K_2CO_3.

Determining the percentage purity by mass on industrial scale acids and bases

24. A NaOH solution prepared industrially has a density of 1.6 gcm^{-3}. 20 mL of this solution required to neutralised with 200 mL of 1 mol dm^{-3} HCl solution. Determine the NaOH in the original solution as a mass percentage.

25. The percentage purity of a HNO_3 solution is 12 % by weight. 20 mL of this solution is neutralised using 30 mL of 0.50 mol dm^{-3} KOH solution. Calculate the density of the HNO_3 acid sample.

26. A certain $Ca(OH)_2$ solution has a density of 1.025 g cm^{-3}. This contains 1.48% $Ca(OH)_2$ by mass. Calculate the volume of 0.1 mol dm^{-3} HCl required to neutralise 25.0 mL solution above. (Ca = 40, H =1, O = 16)

Calculating the number of mols of H_2O in a hydrated salt.

27. Washing soda has the chemical formula of $Na_2CO_3.xH_2O$. 4.29 g of this was dissolved in water to make a 250 mL solution. The volume of 0.2 mol dm^{-3} HCl required to completely react with 25 mL of this solution is 15.0 mL. If methyl orange was used as an indicator, calculate the value of x.

28. Hydrated cobalt chloride has the formula of $CoCl_2.xH_2O$. 7.14 g of hydrated crystals were dissolved to prepare 500 mL solution. 50 mL of this solution was reacted with excess $AgNO_3$ solution. Resulted precipitate was filtered, dried, and weighed to form a 0.861 g precipitate. Determine the value of x. (Ag = 108, Cl = 35.5, Co =59, O =16, H =1)

Quantitative Chemical Analysis

Any material is to be analysed for two aspects: Qualitative and Quantitative. In qualitative analysis chemical species are identified and in quantitative analysis the amounts are identified. For GCE Als there are two techniques that require elaboration.

1. Gravimetric methods
2. Titrimetric methods

Gravimetric method of analysis

This technique involves in the measurement of the weight of a know compound formed during a reaction. For example, a mixture of Na_2CO_3 and $NaHCO_3$ can be analysed using a thermal decomposition method. Ionic compounds can be dissolved and allowed to be reacted with another compound to form precipitates. The mass of this precipitate can be used to analyse an unknown compound too.

Calculations using the gaseous product evolved during a reaction.

29. A mixture of K_2CO_3 and $MgCO_3$ is 2 g in mass. When this mixture was heated until there is a constant mass, the mass loss was 0.88 g. Calculate the mass percentage of $MgCO_3$.

30. A 4.08 g of a mixture containing $MgCO_3$ and $CaCO_3$ was heated at 600 ℃ until there is a constant mass. If the remaining mass is 3.20 g, calculate the mass of $MgCO_3$. (Mg =24, Ca =40, O =16)

31. When CaC_2O_4 is heated, it is decomposed according to $CaC_2O_4(s) \longrightarrow CaCO_3(s) + CO(g)$. 2.00 g of pure CaC_2O_4 undergoes partial decomposition to yield a mass of 1.78 g. This product contains $CaCO_3$ and undecomposed CaC_2O_4. Calculate the mass of undecomposed CaC_2O_4 in the sample.

32. A piece of pure magnesium was completely burnt in a mixture of N_2 and O_2, and mixture of MgO and Mg_3N_2 so obtained had a mass of 1.8 g. when this mixture was heated with excess water, and the product obtained ignited, only MgO was formed. The mass of this MgO was 2.0 g.

1) Write balanced equations for all the relevant reactions. (Ignore the reaction between MgO and H_2O)
2) Calculate the mole ratio MgO: Mg_3N_2 in the mixture formed by burning the piece of magnesium. (R.A.M: Mg = 24, O = 16, N = 14)

33. $CrO_3(s)$ when heated decomposes to give $Cr_2O_3(s)$ and $O_2(g)$ as the only products. 0.4000 g of a sample of CrO_3 contaminated with Cr_2O_3 when heated gave 0.3184 g of Cr_2O_3. Calculate the mass percentage of CrO_3 in the sample. (Cr = 52, O = 16)

Determining the molar ratio of two components in a mixture.

34. $CaCO_3$ and $MgCO_3$ powders were mixed in 1:x molar ratio. There are no other materials in it. 1.30 g of this mixture was completely heated until it is converted to CaO and MgO. The mass of the oxide mixture is 0.64 g. Relative atomic masses are given below. (Ca = 40, Mg =24, C =12)
Consider the following mathematic expression

$$\frac{100 + P \times x}{Q + R \times x} = \frac{1.30g}{S}$$

a. Determine the values for P, Q, R and S.
b. By substituting suitable values determine the value of x.

35. 0.614 g of a mixture containing $KClO_3$ and $NaBrO_3$ was thermally dissociated to remove O_2. The mass loss of the mixture was 0.24 g. Calculate the mole percentage of $KClO_3$. (Br = 80, K = 39, Na =23)

36. There is only $CaCO_3$ and KNO_3 in a mixture. 0.301 g of this sample was thermally decomposed to form a solid residue of 0.197 g. Calculate the molar ratio of CO_2: O_2 in the gaseous mixture. (K =39, Ca = 40)

37. A mixed alloy contains only Ni and Ag. 2.31 g of this mixture was heated with S to form NiS and Ag_2S mixture. The mass of this sulphide mixture is 3.55 g. Calculate the molar ratio of Ni:Ag in the mixture. (Ni -59, Ag-108, S-32)

38. 1. Why is it impossible to use solid NaOH to prepare a solution with an accurate concentration?

2. 100 mL HNO_3 acid containing 6.3 g was titrated with 25.0 mL of NaOH solution. Burette readings obtained on several occasions are given below.

Trial Number	Initial burette reading/ mL	Final burette reading/ mL
1	3.00	30.60
2	2.00	29.00
3	4.80	31.70
4	2.05	29.15

I. Write down two indicators that could be used for this titration and their colour changes at the end point.
II. Using the average values calculate the concentration of NaOH solution in mol dm^{-3}.
III. Determine the volume of 0.1 mol dm^{-3} NaOH solution that can be prepared using 200 mL of the NaOH solution above.

39. 1.2 g of a mixture of anhydrous Na_2CO_3 and NaCl was dissolved in water and a solution of 250 mL was made. It requires 20 mL of 0.1 mol dm^{-3} HCl solution to completely neutralise a 25 mL solution. Calculate the mass percentage of NaCl in the mixture.

40. 50.0 mL of an acid mixture containing HNO_3 and HCl was titrated with 6.25 mol dm^{-3} NaOH. The end point was observed when 42 mL of NaOH was used. When another 50 mL sample of the acid mixture was treated with $AgNO_3$, 2.45 g of AgCl solid was formed. Calculate the concentrations of HNO_3 and HCl. (Ag= 108, Cl = 35.5)

41. 7.14 g of the hydrated $CoCl_2.xH_2O$ was dissolved in water to prepare a solution of 500 mL sample. Excess $AgNO_3$ was added to 50 mL of this solution and the precipitate so obtained has a mass of 0.861 g. Calculate the number of mols of water associated with 1 mol of $CoCl_2$. (Ag -108, Cl-35.5, Co-59, O-16, H-1)

42. 1 g of washing soda ($Na_2CO_3.XH_2O$) was mixed with 50 mL of 1 mol dm^{-3} HCl. Once the reaction is completed, the excess acid was neutralised with 1.018 mol dm^{-3} $Ba(OH)_2$. The volume required was 21.13 mL. Calculate the value of x. (Na = 23, O = 16, H =1)

Additional challenging questions for students to who like to explore the depth.

43. 2.74 g of a mixture containing Na_2CO_3 and $NaHCO_3$ mixture was thermally decomposed to form a constant mass of 2.12 g. Determine the molar ratio of Na_2CO_3 : $NaHCO_3$. (1:2)

44. The metal M forms a divalent chloride, this chloride forms a hydride too. It contains 14.75 % H_2O by mass. 0.1830 g of the hydrate was dissolved in water and treated with $AgNO_3$ to form 0.2145 g of AgCl. (Cl = 35.5, H=1, O=16, Ag=108)

   a. Calculate the relative atomic mass of M (138)
   b. Calculate the number of mols of H_2O in cooperated in each 1 mol of M. (2)

45. 5.72 g of $Na_2CO_3.XH_2O(s)$ was heated until there is a constant mass. This residue weighs 2.12 g. Calculate the value of x in the formula given above. (x=10)

46. A mixed alloy contains on Ni and Ag. 0.285 g of this mixture was heated with excess S to react completely. S unreacted was removed completely by heating the sample. The resulting sulphide mixture weigh 0.397 g. Calculate the molar fraction of Ag. (Ni- 59, Ag- 108, S-32) ($X_{Ag} = \frac{1}{4}$)

47. 0.383 g of a mixture containing $CaCO_3(s)$ and $(NH_4)_2CO_3$ mixture was completely heated to undergo total thermal decomposition. The residue remaining has a mass of 0.056 g. Calculate the molar ratio $CaCO_3(s)$: $(NH_4)_2CO_3$ in the initial mixture. (1:3)

48. 2.84 g of a mixture which contain $MgCO_3$ and $CaCO_3$ was heated together until the total mass is 1.52 g. (Mg =24, C = 12, O =16 and Ca = 40) Calculate the following.

   a. Taking the mass of $MgCO_3$ as x g, determine the mass percentages of the two components.
   b. Calculate the $MgCO_3$:$CaCO_3$ molar ratio using this data.
   c. Calculate the molar fraction of $CaCO_3$.
   d. Calculate the molar percentage of $CaCO_3$. (66.7%)

49. A mixture of NaBr and KBr was dissolved in dil HNO_3 and $AgNO_3$ was added in excess. 0.325 g of the mixture yielded 0.564 g of AgBr. Calculate the mole percentage of KBr in the mixture. (33.33%)

50. A mixture contains $(NH_4)_2CO_3$(s), $CaCO_3$(s) and SiO_2(s). $CaCO_3$:SiO_2 molar ratio is 1:2. 2.68 g of this mixture was heated to a high temperature to form a solid residue of 1.76 g. Calculate the mass of each component in the initial mixture. (Ca =40, N=14, H=1, C=12, O=16, Si=28) {$CaCO_3$ = 1g, SiO_2= 1.2 g)

51. A mixture containing $Na_2CO_3.10H_2O$ and Na_2CO_3 were heated until there is a constant mass. The total mass loss is 2.90 g. Out of this mass loss 1.10 g is due to CO_2. Calculate the mass percentage of $Na_2CO_3.10H_2O$ in the initial mixture. (50. 53 %)

52. A 3.15 g $Ba(OH)_2.XH_2O$ was dissolved in water and was diluted up to 100 mL. 25.00 mL of this solution was titrated with HCl and it required 25.00 mL of 0.2 M HCl for complete neutralisation. (Ba = 137; O = 16; H = 1)

(1) Calculate the value for x.
(2) What is the volume of 0.2 M H_2SO_4 to completely neutralise 25 mL of the above solution?
(3) It required 20 mL of H_3PO_4 to completely neutralise a 25 mL of the above solution. Calculate the concentration of the above solution.

53. The active ingredients in an antacid tablet contained only calcium carbonate and magnesium carbonate. Complete reaction of a sample of the active ingredients required 41.33 mL of 0.0875M hydrochloric acid. The chloride salts from the reaction were obtained by evaporation of the filtrate from the titration; They weighed 0.1900 g. What was the percentage by mass of calcium carbonate in the active ingredients of the antacid tablets?

54. (i)The density of an aqueous solution prepared using pure Na_2CO_3 was found to be 1.0212 g cm^{-3}. Calculate the concentration of this solution. Assume that the density of water at the very same temperature is 1.000 g cm^{-3} and that there is no change in volume during the dissolution of Na_2CO_3.

(II) With the solution in (I) above (in the burette) 25.00 cm^3 aliquots of a H_2SO_4 solution were titrated using phenolphthalein as the indicator. The average of three appropriate end points was 12.50 cm^3. Calculate the concentration of H_2SO_4 solution.

(III) Would it be possible to carry out the above titration in the same way using methyl orange as the indicator? If yes, what is the end point you expect? If no, give reasons. (Na = 23, C = 12, O = 16)

55. The mixtures A and B are identical in colour and colour intensity.

Mixture A	5 mL of tube well water	5 mL of distilled water	5 mL of 0.001 M Salicylic acid
Mixture B	1.5 mL of 0.002 M Fe^{+2} ion solution	8.5 mL of distilled water	5 mL of 0.001 M Salicylic acid

(1) Calculate the concentration of the Fe^{+3} in the tube-well water and give it in mg dm^{-3} (Fe = 56)
(2) What is the colour of the complex formed between Fe^{+3} ions and salicylic acid?

What is the stoichiometric ratio between Fe^{+3} ions and salicylate ions in the above-mentioned complex.